The Effect of the Catalyst on the Mono-Esterification Rate of Phthalic Anhydride by Alcohols

AUTHOR(S):

Tarama, Kimio; Ishibashi, Tetsuji; Nakakawaji, Akira

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26. The Relation between Fluorescence and Chemical Constitution of Organic Compounds

Zen-ichi Yoshida, Yukiyasu Shimada and *Ryohei Oda*

(Oda Laboratory)

Fluorescence of naphth [1, 2] imidazoles and perimidines, which were described in the previous report was compared in alcoholic solution with that of the standard solution of certain organic fluorescent compound under ultraviolet light (3650Å). The results were as follows:

1. Emissivity of fluorescence of naphth [1, 2] imidazole ring was larger than that of perimidine ring.
2. The introduction of conjugated system to 2-position of naphth [1, 2] imidazole increased the emissivity of fluorescence to some extent.
3. The introduction of conjugated system to 2-position of perimidine showed scarcely any effect.

These results are well explained according to our theory (Memoirs of the Faculty of Engineering, Kyoto University, **13**, 108–122 (1951)) and Hirschberg (J. Am. Chem. Soc. **72**, 5117 (1950)).

Synthesized naphth [1, 2] imidazoles are useful for optical bleaching agent, since they emit blue violet~greenich blue strong fluorescent light.

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27. The Effect of the Catalyst on the Mono-Esterification Rate of Phthalic Anhydride by Alcohols

Kimio Tarama, Tetsuji Ishibashi and *Akira Nakakawaji*

(Kodama Laboratory)

We newly found that the mono-esterification rate of phthalic anhydride by alcohol was accelerated by the addition of HCl, and these catalytic reaction rates for propyl-, butyl-, isobutyl- and cyclohexyl-alcohol were respectively investigated in detail.

The reaction rate was the first order with respect to the concentration of phthalic anhydride by using alcohol in excess, and a part of observed rate constants k_1 is shown in Table 1.

Table 1. First-order rate constants k_1.

Phthalic Anhydride 0.1M; Benzene: Alcohol=7:3 (vol.)

Butyl Alcohol		Isobutyl Alcohol		Propyl Alcohol		Cyclohexanol	
Conc. of HCl (mol/l)	$k_1^{35°}$ (hr^{-1})	Conc. of HCl (mol/l)	$k_1^{35°}$ (hr^{-1})	Conc. of HCl (mol/l)	$k_1^{35°}$ (hr^{-1})	Conc. of HCl (mol/l)	$k_1^{75°}$ (hr^{-1})
0	0.0565	0	0.0302	0	0.0557	0	0.0518
0.010	0.145	0.010	0.108	0.010	0.111	0.011	0.169
0.020	0.245	0.020	0.182	0.020	0.208	0 021	0.281
0.030	0.347	0.030	0.279				

The values of these k_1 are proportional to the quantity of added HCl, according to the following relation.

$$k_1 = k_0 [ROH] + k_{HCl} [ROH_2^+]$$

$$[ROH_2^+] \fallingdotseq [HCl]$$

From this equation, the second order rate constants k_0 (by no catalyst) and k_{HCl} (by HCl catalyst) are calculated, and the values of k_0 are in good accordance with the values which were obtained experimentally without catalyst. k_{HCl} at 35°C are given in Table 2. Because these values of k_{HCl} are about 10^2 times larger than the rate constants of the di-esterification of monoester by HCl catalyst, the di-esterification may be negligible in this experimental condition. These are the results when the mixture of benzene and alcohol of 7:3 in vol. ratio was used as the solvent. In the case of the solvent containing the smaller amount of benzene, k_0 became somewhat larger, but the value of k_{HCl} was little affected.

From the temperature dependence of k_{HCl}, the activation energies E and the frequency factors A are obtained as shown in Table 2.

Table 2.

The values of $k_{HCl}^{35°}$, activation energies E and logA.

Alcohol	$k_{HCl}^{35°} \times 10^3$ (1/mol.·sec.)	E (kcal.)	logA
Propyl	1.95	13.4	6.84
Butyl	2.69	14.8	8.32
Isobutyl	2.24	14.3	7.50
Cyclohexyl	0.309*	12.3	5.21

* Extrapolated

In comparison with the results by no catalyst, E's are almost equal, but A's are remarkably large.